AD-A280 830

OFFICE OF NAVAL RESEARCH

SYNTHESIS OF WELL DEFINED POLYMERS BY RADICAL POLYMERIZATION

by

S. Gaynor, D. Greszta, T. Shigemoto, D. Mardare, K. Matyjaszewski

Published

DTIC
ELECTE
S **.JUN 3 0 1994** **D**
F

in the

ACS Polym. Preprints, in press

Carnegie Mellon University
Department of Chemistry
4400 Fifth Avenue
Pittsburgh, PA 15213

June 30, 1994

94-20040

94 6 29 101

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	June 30, 1994	Technical Report #6

4. TITLE AND SUBTITLE
Synthesis of Well Defined Polymers By Radical Polymerization

5. FUNDING NUMBERS
N00014-94-1-0101

6. AUTHOR(S)
Scott Gaynor, Dorota Greszta, Takeo Shigemoto, Daniela Mardare, Krzysztof Matyjaszewski

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Carnegie Mellon University
Department of Chemistry
4400 Fifth Avenue
Pittsburgh, PA 15213

8. PERFORMING ORGANIZATION REPORT NUMBER
N00014-94-1-0101

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Department of the Navy
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
Technical Report #6

11. SUPPLEMENTARY NOTES
ACS Polym. Preprints, in press

12a. DISTRIBUTION/AVAILABILITY STATEMENT

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Several approaches to synthesis of polymers with controlled molecular weights, desired end groups and low polydispersities, by controlled radical polymerization are discussed. The first one is based on nitroxyl radicals such as TEMPO which can react reversibly with propagating radicals. The position of the equilibrium constant depends on the nature of the radical, solvent and temperature. Polymerization rates in systems involving polar monomers (methyl methacrylate, methyl acrylate, vinyl acetate) are higher than in systems based on non-polar monomers (styrene). Other systems involve persistent organometallic-based radicals or hypercoordinated organic radicals as dormant species, in equilibrium with propagating macroradicals.

14. SUBJECT TERMS	15. NUMBER OF PAGES
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Classified	Classified	Classified	UL

SYNTHESIS OF WELL DEFINED POLYMERS BY RADICAL POLYMERIZATION

Scott Gaynor, Dorota Greszta, Takeo Shigemoto,
Daniela Mardare and Krzysztof Matyjaszewski*

Department of Chemistry
Carnegie Mellon University
4400 Fifth Avenue
Pittsburgh, PA, 15213

Introduction

Polymers with controlled molecular weights, desired end groups and low polydispersities are usually prepared by living polymerization. Living polymerization is a chain growth process without transfer and without termination. Additionally, the preparation of polymers with predetermined molecular weights and narrow molecular weight distribution requires fast initiation and fast exchange between sites of variable activities and variable lifetimes [1]. Bimolecular termination between two growing radicals cannot be avoided, at least in homogenous radical polymerization, and therefore living radical polymerization cannot be fully realized. Moreover, in most radical systems initiation is slow and high molecular weight polymers are formed at the very beginning of the reaction, and subsequently molecular weights decrease and polydispersities increase. However, it is possible to adjust conditions of radical polymerization in a way which enables preparation of polymers with controlled molecular weights and relatively low polydispersities [2]. Such systems are not living per se because termination reactions do occur but have some characteristics of living systems and therefore should be called either "living" or controlled, since they provide polymers with controlled molecular weights and controlled molecular weight distributions.

There are several approaches to the controlled radical polymerization. Physical methods based on the heterogeneous systems [3] will not be discussed here. Homogenous radical systems with some characteristics of "living" systems such as an increase of molecular weights with conversion, relatively low polydispersities, ability to form block copolymers may be based on the reversible deactivation of growing radicals. In a recent review [2], these systems have been divided into three categories:

1. Deactivation of a growing radical with a stable radical by the reversible formation of a dormant covalent species, followed by their homolytic cleavage:

$$P\text{\textbullet} + R\text{\textbullet} \underset{k_{act}}{\overset{k_{deact}}{\rightleftharpoons}} P\text{-}R \qquad (1)$$
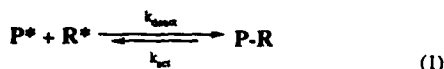
2. Reversible deactivation of a growing radical with a "non-radical" species by the formation of a dormant persistent radical:

$$P\text{\textbullet} + X \underset{k_{act}}{\overset{k_{deact}}{\rightleftharpoons}} \{P\text{-}X\}\text{\textbullet} \qquad (2)$$
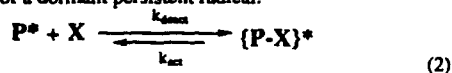
3. Reversible degenerative transfer based on the thermodynamically neutral exchange reactions between growing radicals and transfer agents:

$$P_n\text{\textbullet} + P_1\text{-}R \overset{k_{tr}}{\rightleftharpoons} P_1\text{\textbullet} + P_n\text{-}R \qquad (3)$$
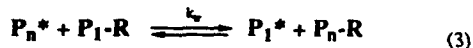
In the first category, various nitroxyl radicals, protected phenoxyl radicals, dithiocarbamate, trityl and benzhydryl derivatives have been used with variable success. The second category is generally based on the organometallic compounds which form stabilized hypercoordinated radicals. The third group requires very rapid and "clean" transfer without any side reactions.

The enhanced control of a polymerization process originates in:
- reduction of the ratio of the rate of termination to that of propagation, due to low instantaneous concentration of growing radicals;
- similar rates of initiation and propagation due to application of the initiators resembling polymer end groups in their dormant state;
- low proportion of chains marked by uncontrolled termination and/or transfer due to relatively low molecular weights.

Below we will discuss some systems which allow synthesis of controlled polymers by radical polymerization.

Results and Discussion

1. Deactivation by Nitroxyl Radicals

Various stable radicals react with growing radicals according to eq. 1. The main advantage of nitroxyl radicals in comparison with dithiocarbamate, galvinoxyl, verdazyl, benzhydryl and trityl derivatives is that they do not initiate polymerization by addition to double bonds and they react selectively with growing radicals to form reversibly covalent species (e.g. aromatic rings are not attacked) [4]. Additionally, reaction of growing radicals with dormant species occurs via degenerative transfer:

$$P_n\text{\textbullet} + R'_2N\text{-}O\text{-}R \rightleftharpoons P_n\text{-}O\text{-}NR'_2 + R\text{\textbullet} \qquad (4)$$
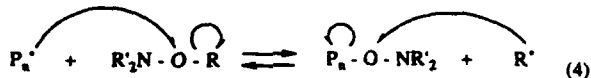
and not via irreversible formation of the head-to-head linkages (degradative transfer) as observed for dithiocarbamate derivatives [5]:

$$R_2N\text{-}C(S)S\text{-}P_n + P_m\text{\textbullet} \longrightarrow R_2N\text{-}C(S)S\text{\textbullet} + P_n\text{-}P_m \qquad (5)$$
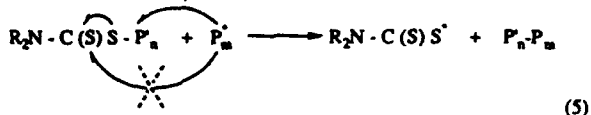
Nitroxyl radicals such as TEMPO react reversibly with propagating radicals. The position of the equilibrium constant depends on the nature of the radical, solvent and temperature. There are several approaches to controlled initiating systems. The first one is based on using alkoxyamines prepared in advance. They can be used alone or together with a small amount of the typical radical initiators such as peresters or azo compounds[6]. Alkoxyamines can be also prepared in situ by adding a radical initiator in concentrations comparable to the nitroxyl radicals [7]. The optimal amount of the radical initiator depends on the efficiency of the initiation and ideally the concentration of the radicals generated from the initiator should be slightly higher than concentration of the scavenger. Alkoxyamines can be also formed without initiator, for example during thermal polymerization of styrene [8].

After the initial non-stationary period, a typical alkene polymerization in the presence of alkoxyamines proceeds according to the first order kinetics with the monotonous increase of molecular weights with conversion. Polydispersities and the contribution of the non-stationary period depend on temperature, particular initiating system and the nature of monomers (electron-donating or electron-accepting), as shown in Figures 1 and 2.
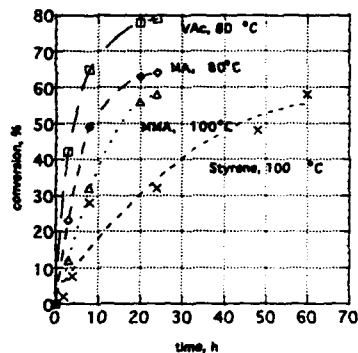

Fig. 1 Time-conversion plots in radical bulk polymerization of styrene, methyl methacrylate (MMA), methyl acrylate (MA), and vinyl acetate (VAc) initiated by AIBN(0.03M)/TEMPO(0.03M).

Polymerization rates in systems involving polar monomers (methyl methacrylate, methyl acrylate, vinyl acetate) are higher than in systems based on non-polar monomers (styrene), at comparable temperatures. The polymerization rates depend on the position of equilibrum (eq. 1) and also on the amount of radicals formed from the initiator which is related to the efficiency of initiation.
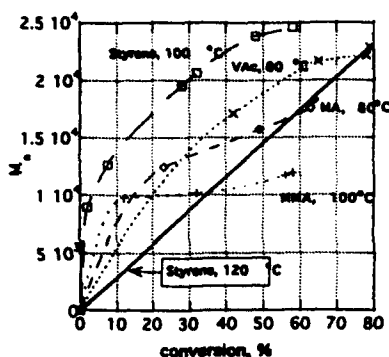
Fig. 2 M_n-conversion dependence in radical bulk polymerization of styrene, methyl methacrylate (MMA), methyl acrylate (MA), and vinyl acetate (VAc) initiated by AIBN(0.03M)/TEMPO(0.03M).

Molecular weights are initially higher than predicted from the number of scavenger molecules. This indicates incomplete trapping of radicals and slow exchange reactions. By contrast, at higher temperature (styrene, 120°C), ideal behaviour is observed. Polydispersities, M_w/M_n, are higher than 2. This broadening of molecular weight distributions might be attributed to the slow homolytic cleavage of the alkoxyamine-capped dormant chains, and to the slow bimolecular degenerative transfer reactions involving dormant chains and growing propagating macroradicals. At higher temperatures (styrene, 120°C), polydispersities are much lower ($M_w/M_n < 1.3$), indicating sufficiently high exchange rates.

2. Polymerization in the Presence of Organometallic Compounds

Some organometallic compounds react reversibly with alkyl radicals according to eq. 2. This reversibility can be successfully employed for the controlled radical polymerization. There are two potential side reactions which limit use of the organometallic species. The first one is β-hydrogen abstraction from the growing radical and formation of metal hydrides (eq. 6):

$$R\text{-}CH_2\text{-}CH_2\text{-}Mt.Llg \longrightarrow R\text{-}CH=CH_2 + Llg.Mt\text{-}H$$

$$Mt = Co, Rh$$

$$(6)$$

Depending on the reactivity of metal hydrides, this reaction can be considered either as transfer or termination. Organocobalt derivatives are commercially used as very efficient transfer agents in polymerization of methyl methacrylate [9,10]. Apparently, they are much less efficient in polymerization of monosubstituted alkenes such as styrene and acrylates since monomer contribution on transfer is much smaller and polymers with enhanced degree of control can be obtained.

Another side reaction in these systems could be an electron transfer or heterolytic cleavage of the metal-carbon linkage. In that case, metal can be oxidized and anionic growing species can be formed. This reaction is especially facile for monomers with electron withdrawing substituents, e.g. (meth)acrylates (eq.7):

$$P_n\text{-}CH_2\text{-}C\text{-}Mt^{n\bullet} \longrightarrow P_n\text{-}CH_2\text{-}C^- + Mt^{n+1}$$

(with CH_3, $C=O$, OCH_3 substituents)
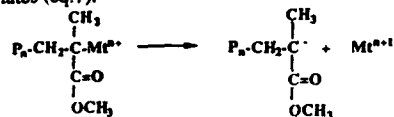
$$(7)$$

These side reactions can be, however, suppressed. The affinity of a metal to hydrogen abstraction, and/or its ability to lose electrons depend on the nature of metals, their oxidation states and nature of ligands. High oxidation state, ligands protecting from the abstraction of the β-H atoms and controlling the position of the oxidation-reduction equilibrium are desired for controlled radical polymerization.

We have previously described controlled polymerization of vinyl acetate in the presence of trialkylaluminum complexed by bipyridyl and activated by stable radicals such as TEMPO[11]. This system allows preparation of block copolymers[12] but is very sensitive to moisture and oxygen. In search for less sensitive systems we investigated various chromium, rhodium, zirconium and cerium derivatives. Nature and concentration of the organometallic compound, ligands and the radical source influence polymerization rates by affecting equilibria between dormant and active species as well as the relative rates of initiation and propagation and contribution of transfer reactions.

Some metallocenes activated by diazonium salts are very efficient initiators for polymerization of electron-donating monomers (e.g. acrylic monomers). Polymerization of electron-accepting monomers (e.g. vinyl acetate, styrene) is, however, poorly controlled with these initiating systems and proceeds better with chromium derivatives solvated by macrocyclic tetra(hexa)aza compounds [13].

We currently study various combinations of organometallic compounds, ligands, and radical sources in polymerization of (meth)acrylates, styrene, vinyl acetate and other alkenes.

3. Other systems

Formation of the persistent phosphorus-based radicals was already described in literature[14]. In the case of the low stability of the hypercoordinated radicals, the ligand exchange becomes facile, therefore some organoaluminum, organoboron, and other compounds have been already successfully used as transfer agents in the polymerization of styrene, acrylates and vinyl acetate[15,16].

We have also used phosphites for this purpose and an increase of polymerization rates in polymerization of vinyl acetate initiated by BPO/tris(trifluoroethyl) phosphite (1 to 1.5-5) was already reported by us[17]. In addition, the phosphite accelerated the decomposition of BPO, used as initiator and provided polymers with relatively low polydispersities and molecular weights depending on the concentration of the initiating system. However, it was found that the phosphite was also incorporated into polymer backbone (≈5%), via copolymerization process to form ...-$CH_2CHR\text{-}P(OR)_3\text{-}CH_2\text{-}CHR\text{-}...$ linkages. Some other elementoorganic compounds are currently being evaluated in our laboratories.

References
1. Matyjaszewski, K., *Macromolecules*, **1993**, *26*, 1787
2. Greszta, D., Mardare, D., Matyjaszewski, K.,*Macromolecules*, **1994**, *27*, 638
3. Harwood, H. J., in "*Encyclopedia of Polymer Science and Technology*", Supplement Volume, Wiley, New York, 1989, p.429.
4. Griffiths P.G., Rizzardo, E., Solomon, D.H., *Tetrahedron Lett.* **1982**, *23*, 1309
5. Lambrinos, P., Tardi, M., Polton, A., Sigwalt, P., *Eur. Polym. J.* **1990**, *26*, 1125.
6. Solomon, D.H.; Waverly, G.; Rizzardo, E.; Hill, W.; Cacioli, P., U.S.Patent, 4,581,429, **1986**
7. Georges, M. K., Veregin, R. P. N., Kazmaier, P. M., Hamer, G. K., *Macromolecules*, **1993**, *26*, 2987
8. Mardare, D., Matyjaszewski, K., *ACS Polym. Preprints*, **1994**, *35(1)*, 778
9. Smirnov, B. R., Morozova, I. S., Puschaeva, L. M., Marchenko, A. P., Enikolopyan, N. S., *Dokl. Akad. Nauk SSSR*. **1980**, *255*, 609
10. Melby, L.R.; Janowicz, A.H.; Ittel, S.D. Eur. Pat. Appl. EP 196,783
11. Mardare, D., Matyjaszewski, K., *Macromolecules*, **1994**, *27*, 645
12. Mardare, D., Matyjaszewski, K., *ACS Polym. Preprints* , **1993**, *34(2)*, 566
13. Mardare, D., Gaynor, S., Matyjaszewski, K., *ACS Polym. Preprints*, **1994**, *35(1)*, 700
14. Davies, A. G., Griller, D., Roberts, B. P. *J. Chem. Soc., Perkin Trans. II*, **1972**, 2229
15. Huff, T., Perry, E. *J. Am. Chem. Soc.* **1960**, *82*, 4277
16. Milovskaya, E. B. *Russ. Chem. Rev.* **1973**, *42(5)*, 1979
17. Greszta, D., Mardare, D., Matyjaszewski, K. *ACS Polymer Preprints* **1994**, *35(1)*, 466.